Are ab initio quantum chemistry methods able to predict vibrational states up to the dissociation limit for multi-electron molecules close to spectroscopic accuracy?

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Motivation

System studied: vibrational and rotational spectrum of LiH

- vibrational levels up to dissociation

Our final goal is to obtain the theoretical vibrational spectrum of O_3, LiH serves as a case study to understand different factors influencing the result.

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Our final goal is to obtain the theoretical vibrational spectrum of O_3, LiH serves as a case study to understand different factors influencing the result.

Accurate theoretical calculation of ro-vibrational levels of molecules requires accurate determination of

- the Born-Oppenheimer (BO) potential energy surface;
- adiabatic correction;
- non-adiabatic effects;
- a precise method for solving the vibrational problem.

The Bunker-Moss Hamiltonian

The non-adiabatic effects (due to the excited states) on the vibrational levels of the ground state are considered in a perturbative fashion:

$$H_{BM} = -\frac{\hbar^2}{2\mu}\frac{\partial}{\partial R}(1+\beta(R))\frac{\partial}{\partial R} + W_{BO}(R) + W_{DBOC}(R)$$

where μ is the reduced nuclear mass; W_{BO} is the Born-Oppenheimer (electronic) potential.

This Hamiltonian differs from the Born-Oppenheimer nuclear Hamiltonian by the β function and the DBOC:

$$\beta(R) = \frac{2\hbar^2}{\mu}\sum_n \frac{\left\langle \Psi_n \left| \frac{\partial}{\partial R} \right| \Psi_0 \right\rangle^2}{E_0 - E_n}$$

$$W_{DBOC}(R) = -\frac{\hbar^2}{2\mu}\sum_{X_A} \left\langle \Psi_0 \left| \left(\frac{\partial^2}{\partial X_A^2} \right)_R \right| \Psi_0 \right\rangle$$

Electronic structure calculation

- Born-Oppenheimer (BO) surface
  - High level electronic structure method (MR-CISD+Q)
  - Extrapolated one-electron basis
  - Reletivistic correction
- Diagonal Born-Oppenheimer correction (DBOC)
- Non-adiabatic effects

BO surface: electron correlation

An *MR-CISD wave function* was constructed using:

- a CAS reference space including 7σ, 3π, 1δ orbitals and all four electrons
- all single and double excitations out of these functions

Size-extensivity correction has been applied:

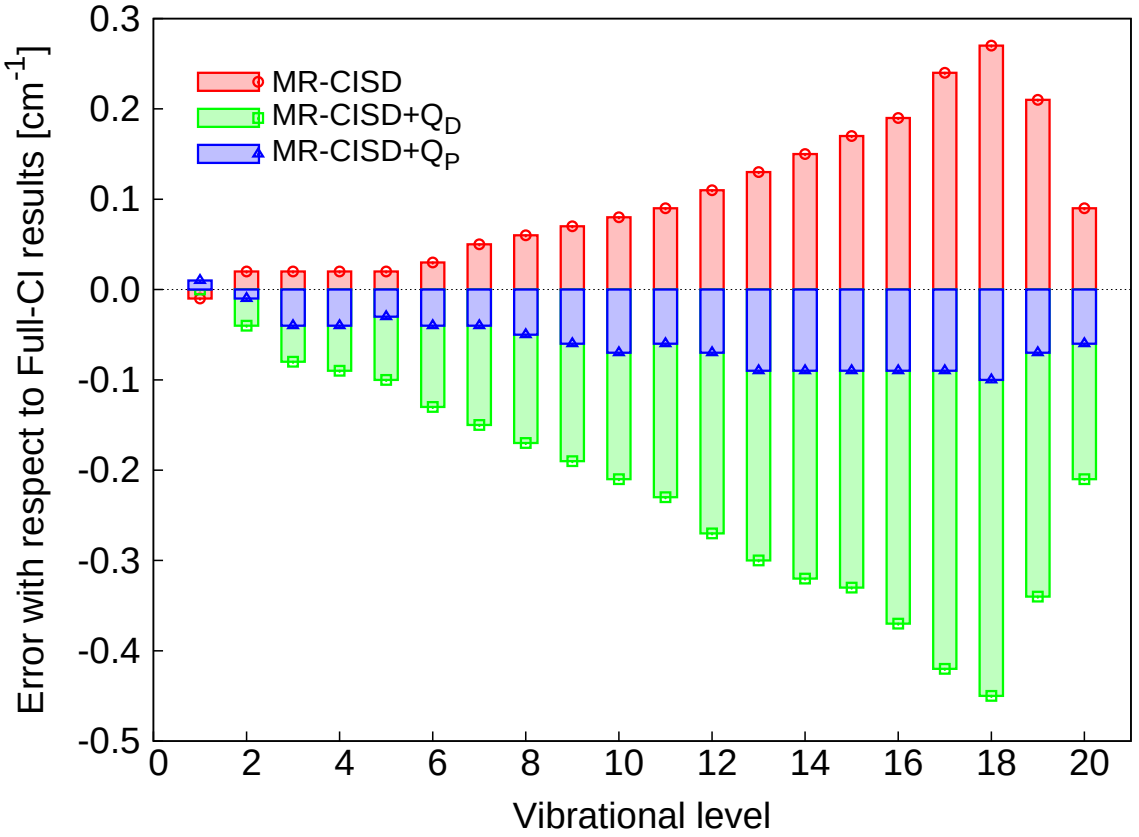
- the original one suggested by Davidson (referred to hereafter as $+\mathrm{Q}$)
- Pople-variant(referred to as $+\mathrm{Q_P}$).

Program:

- COLUMBUS (http://www.univie.ac.at/columbus)

BO surface: electron correlation

Convergence of the calculated vibrational frequencies with respect to full-CI values (pw-CVQZ basis)



BO surface: electron correlation

Dissociation energy (cm^{-1}) and equilibrium bond length (bohr) calculated for potential energy curves obtained by different correlated methods and the pw-CVQZ basis set

Method	MR-CISD	MR-CISD+Q	MR-CISD+Q_P	Full-CI
D_e	20175.50	20175.40	20174.90	20174.90
r_e	3.01383	3.01378	3.01377	3.01381

BO surface: basis set

Li: pw-CVXZ basis sets of Peterson with X=T,Q,5,6

H: usual cc-pVXZ basis set

Note: the largest calculations with the pw-CV6Z basis involve 349 functions!

Basis set extrapolation of the energy:

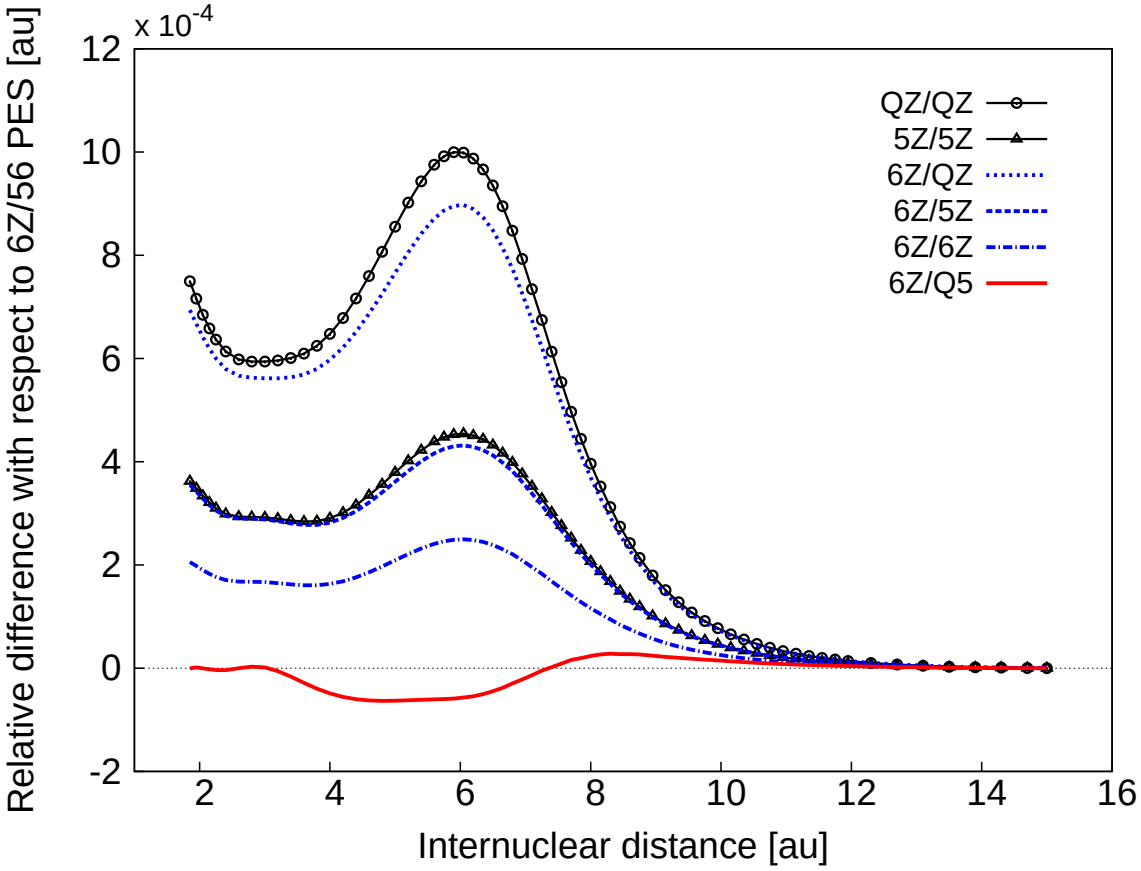
$$E_{corr}(X) = E_{corr}^{\infty} + \frac{a}{X^3}$$

(45) means: extrapolation using QZ and 5Z

(56) means: extrapolation using 5Z and 6Z

BO surface: basis set

Convergence of the potential energy surfaces with the basis set and extrapolation.
Results with respect to the highest level, i.e. (56) extrapolation



BO surface: basis set

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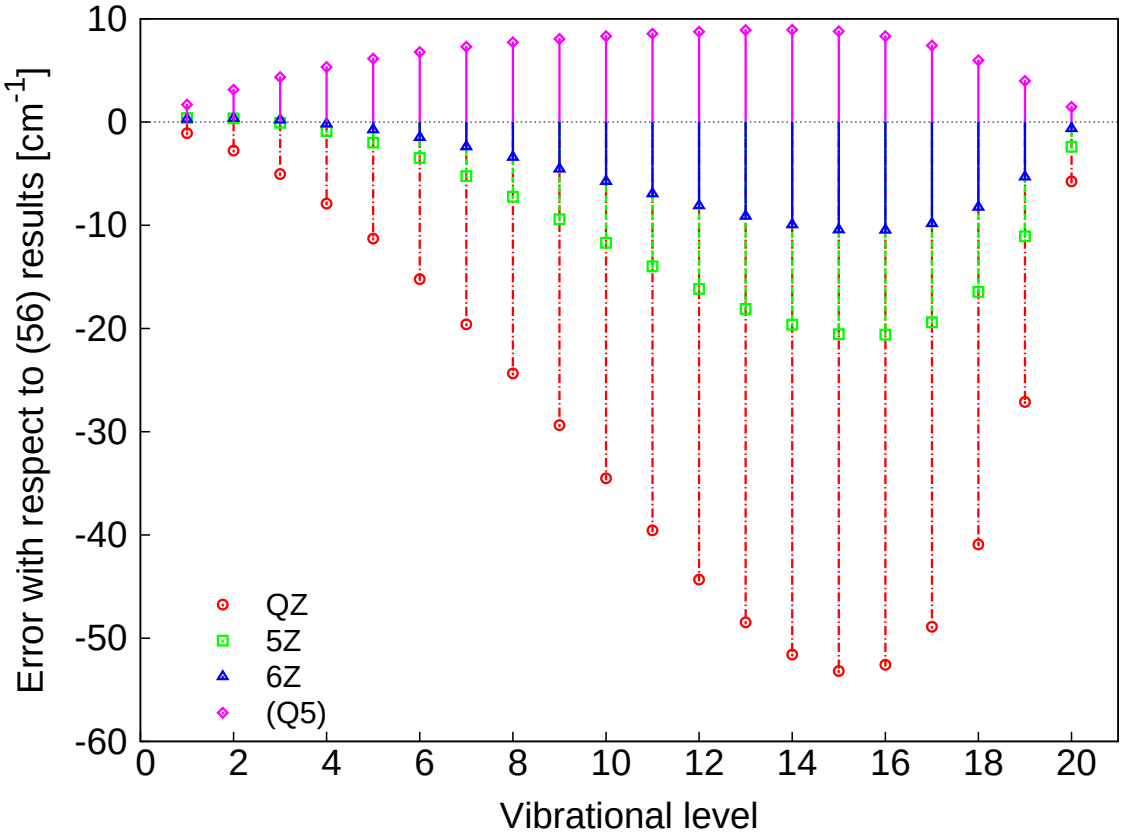


BO surface: basis set

Dissociation energy (cm^{-1}) and equilibrium bond length (bohr) calculated for potential energy curves obtained by different basis sets.

basis	QZ	5Z	(Q5)	6Z	(56)
D_e	20182.14	20242.18	20305.17	20268.85	20305.40
r_e	3.01393	3.01410	3.01428	3.01402	3.01390

Diagonal Born-Oppenheimer Correction (DBOC)

$$W_{DBOC}(R) = -\frac{\hbar^2}{2\mu}\sum_{X_A}\left\langle \Psi_0 \left| \left(\frac{\partial^2}{\partial X_A^2}\right)_R \right| \Psi_0 \right\rangle$$

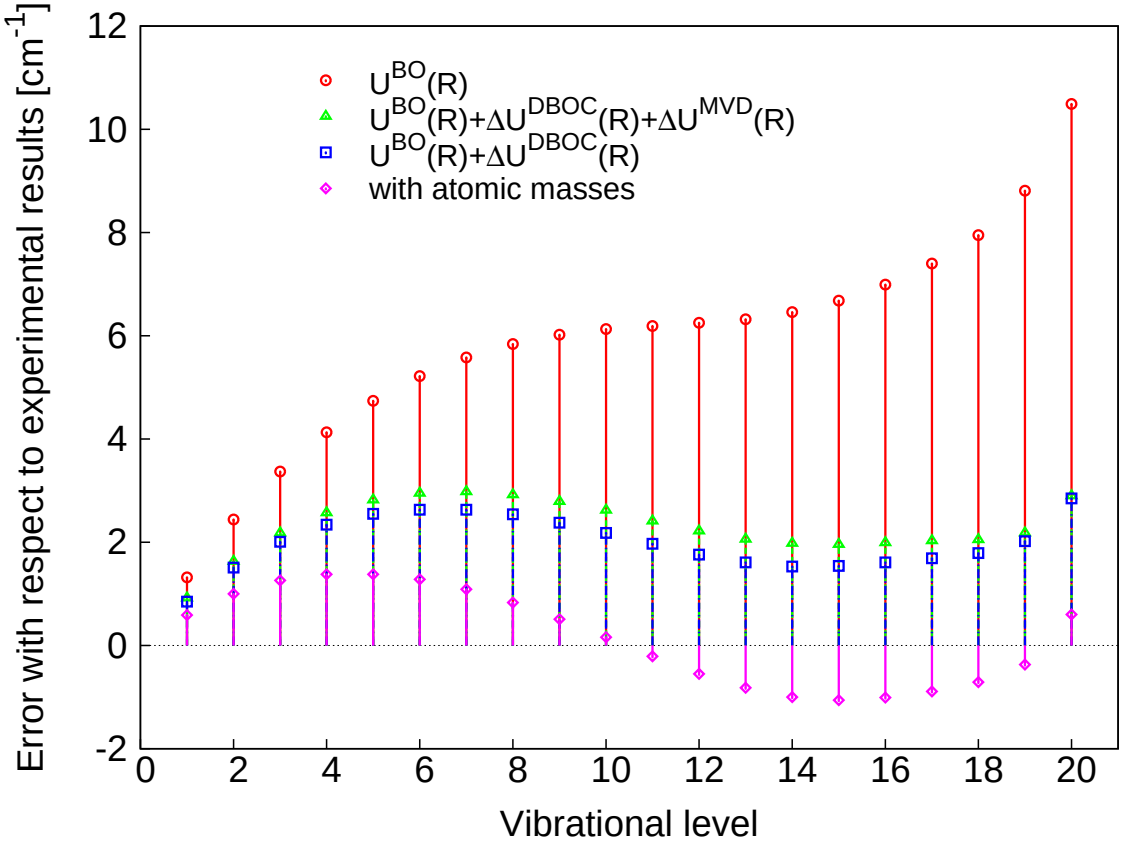
Method:

- DBOC was calculated analytically using the procedure developed by us. Gauss, Tajti, Kállay, Stanton, Szalay, *J. Chem. Phys.*, **125**, 144111 (2006).

Calculations:

- same MR-CISD wave function, pw-CVTZ basis set
- program: MRCC program by Kállay (www.mrcc.hu) coupled to the CFOUR suite (www.cfour.de).

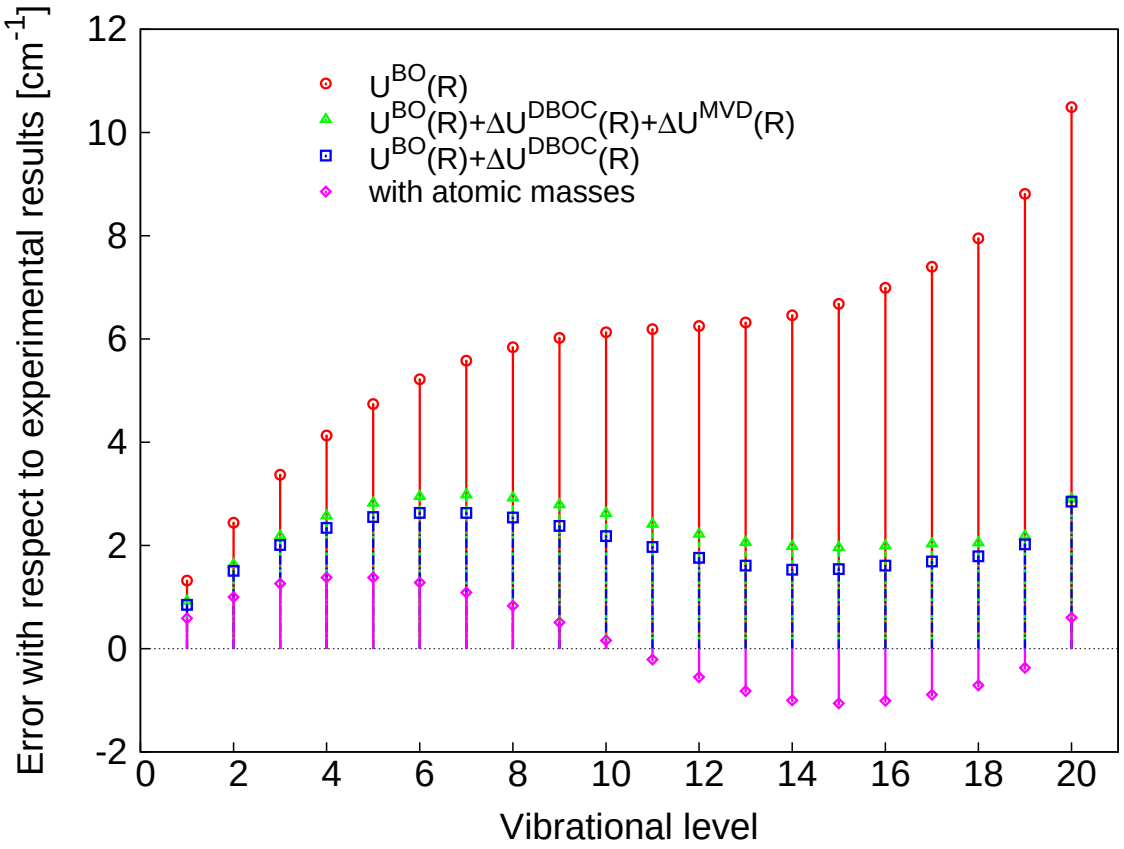
Diagonal Born-Oppenheimer Correction (DBOC)



– DBOC is not at all negligible

– Remaining error due to DBOC is not expected be larger than 0.2 cm^{-1}

Relativistic effects: Mass-velocity Darvin (MVD) correction



– Not important this time

Non-adiabatic effects: coupling with excited states

Two approximate methods:

- inclusion of the non-adiabatic β coupling:

$$\beta(R) = \frac{2\hbar^2}{\mu} \sum_n \frac{\left\langle \Psi_n \left| \frac{\partial}{\partial R} \right| \Psi_0 \right\rangle^2}{E_0 - E_n}$$

- using atomic masses in the vibrational equation (see Kutzelnigg 2007)

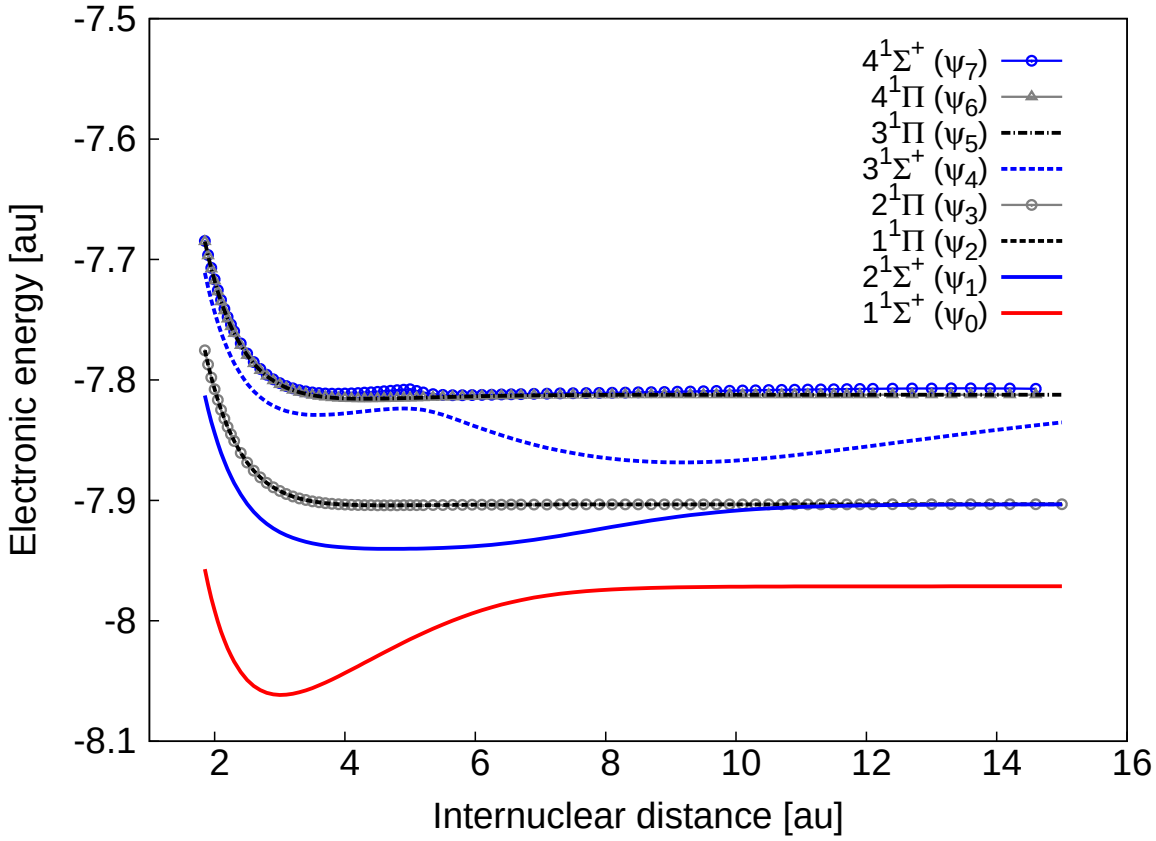
Calculations:

- analytic evaluation by MR-CISD as derived by us
  Lischka, Dallos, Szalay, Yarkony and Shepard, *J. Chem. Phys.* **120**, 7322-7329 (2004).

- Program: Columbus (http://www.univie.ac.at/Columbus)

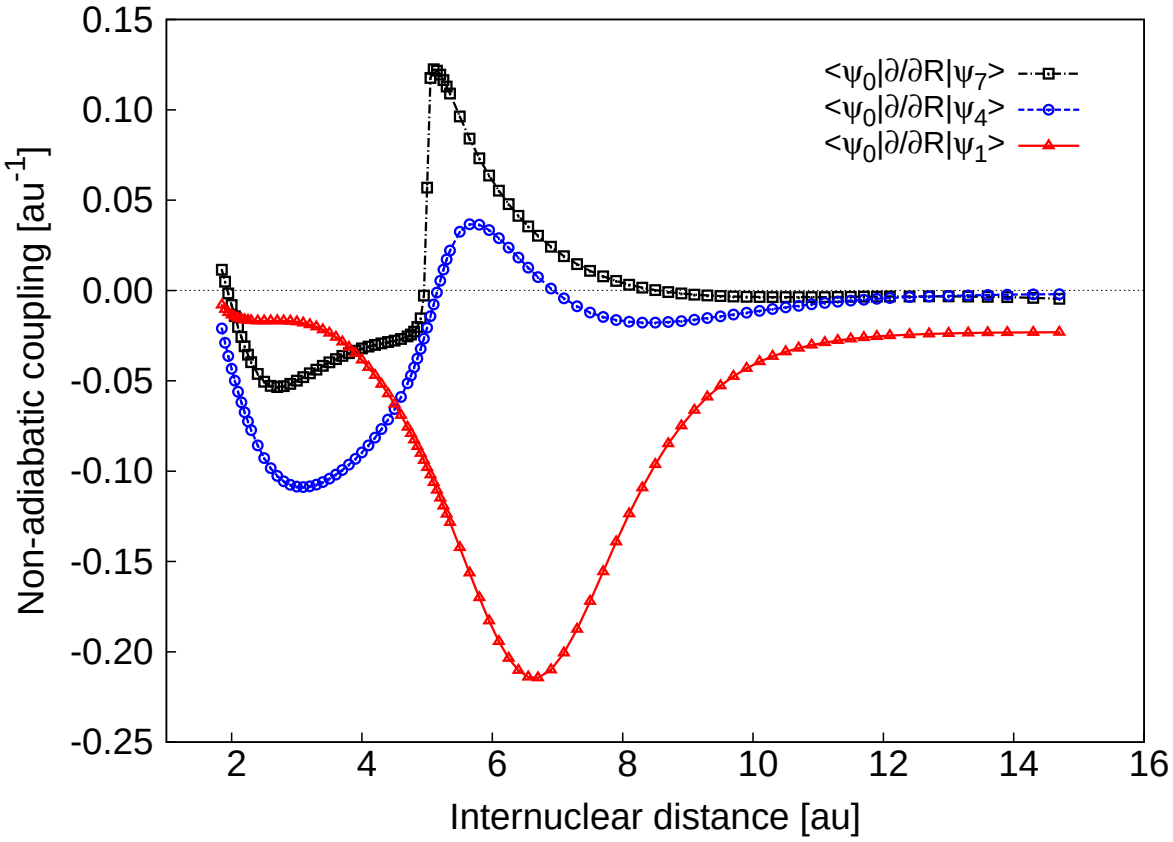
Non-adiabatic effects: coupling with excited states

Potential energy curves for the excited states of LiH



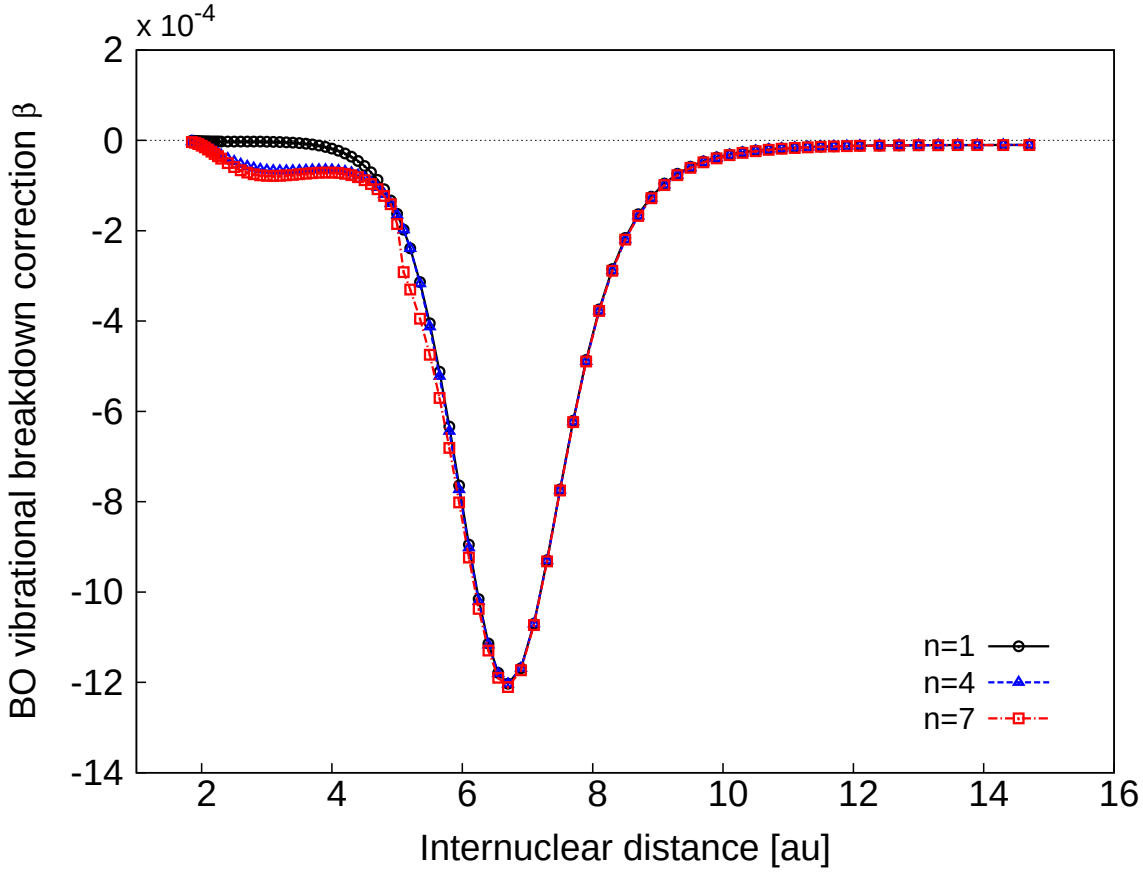
Non-adiabatic effects: coupling with excited states

Non-adiabatic coupling functions

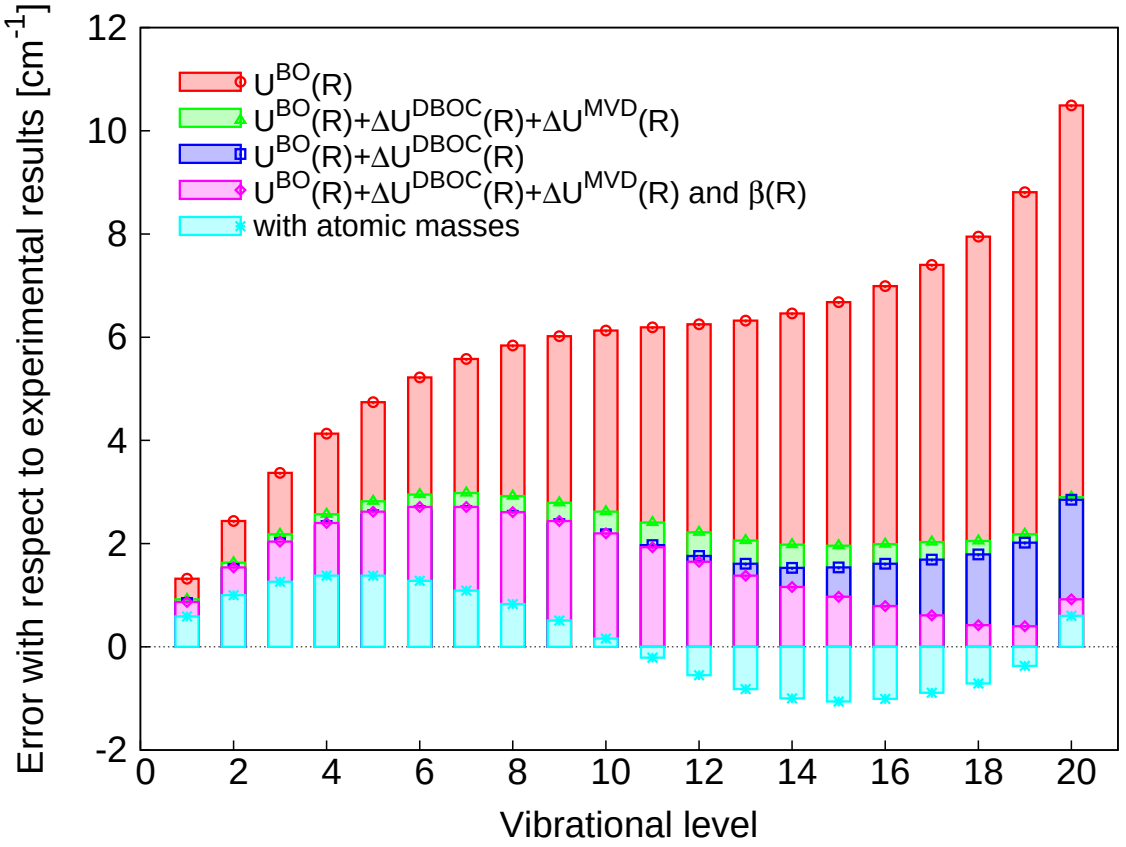


Non-adiabatic effects: coupling with excited states

Cumulative beta function ($\beta(R)$).



Final vibrational results

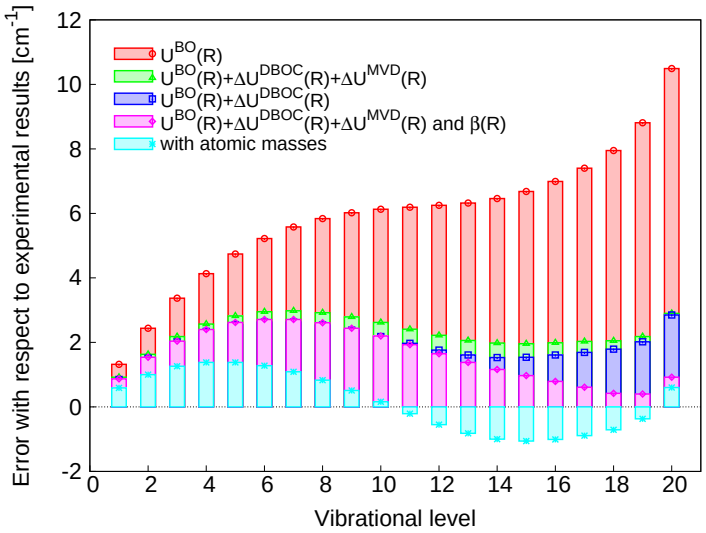


ν	^{7}LiH	Calc.-Emp.	^{6}LiH	Calc.-Emp.	^{7}LiD	Calc.-Emp.	^{6}LiD	Calc.-Emp.
1	1360.30	0.59	1373.96	0.60	1029.51	0.45	1047.95	0.45
2	2675.56	1.00	2701.98	1.03	2033.46	0.79	2069.39	0.78
3	3946.73	1.26	3985.01	1.30	3012.25	1.05	3064.76	1.03
4	5174.66	1.38	5223.92	1.45	3966.27	1.22	4034.47	1.18
5	6360.11	1.38	6419.51	1.47	4895.88	1.32	4978.90	1.26
6	7503.75	1.28	7572.45	1.38	5801.43	1.35	5898.39	1.26
7	8606.13	1.09	8683.29	1.21	6683.20	1.31	6793.26	1.21
8	9667.63	0.83	9752.43	0.97	7541.48	1.23	7663.80	1.09
9	10688.48	0.51	10780.07	0.67	8376.48	1.09	8510.24	0.93
10	11668.68	0.16	11766.21	0.33	9188.39	0.91	9332.76	0.72
11	12607.98	-0.21	12710.53	-0.01	9977.35	0.69	10131.50	0.48
12	13505.75	-0.55	13612.36	-0.32	10743.43	0.44	10906.51	0.21
13	14360.93	-0.82	14470.53	-0.56	11486.63	0.16	11657.79	-0.08
14	15171.87	-1.00	15283.23	-0.69	12206.88	-0.13	12385.23	-0.39
15	15936.14	-1.06	16047.83	-0.70	12904.00	-0.42	13088.61	-0.69
16	16650.32	-1.01	16760.61	-0.61	13577.68	-0.69	13767.56	-0.97
17	17309.68	-0.89	17416.44	-0.45	14227.48	-0.93	14421.57	-1.21
18	17907.81	-0.71	18008.33	-0.24	14852.76	-1.13	15049.91	-1.40
19	18436.12	-0.37	18526.95	0.20	15452.68	-1.28	15651.58	-1.53
20	18883.35	0.60	18960.14	1.44	16026.13	-1.36	16225.30	-1.58
21	(19235.47)		19292.85	3.86	16571.65	-1.38	16769.40	-1.58
22	(19475.88)		(19507.41)		17087.42	-1.36	17281.76	-1.52
23					17571.12	-1.29	17759.69	-1.42
24					18019.83	-1.17	18199.81	-1.26
25					18429.93	-0.96	18597.92	-0.93
26					18796.98	-0.48	18948.88	-0.20
27					19115.60	0.58	(19246.58)	
28					(19379.59)		(19484.03)	
29					(19581.91)		(19653.33)	
30					(19714.95)			

Summary of the vibrational calculations

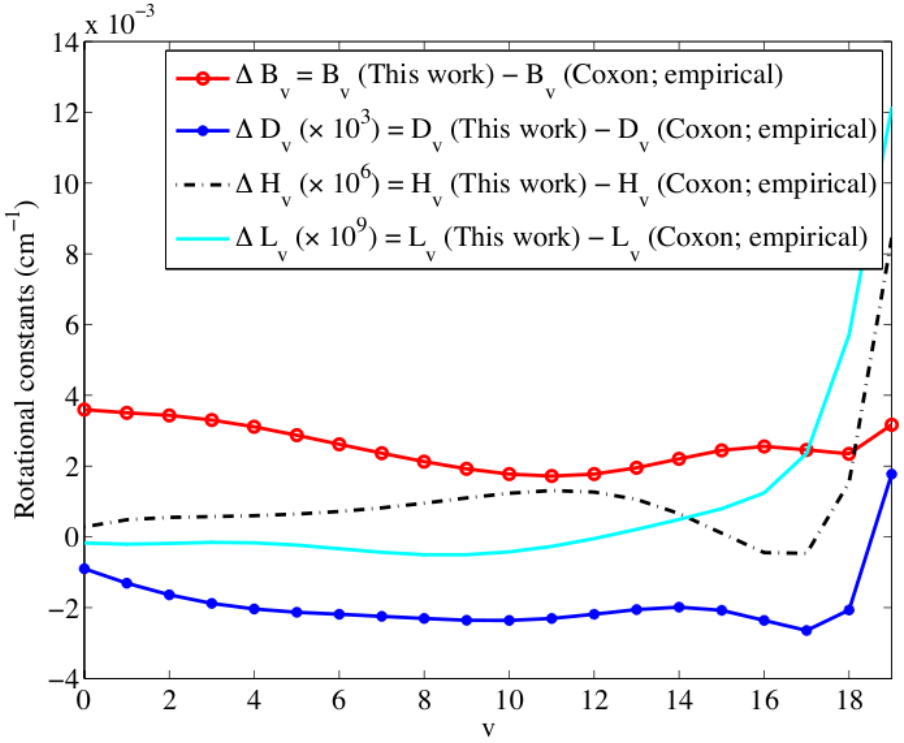
RMS deviations between *ab initio* and empirical values of vibrational energies.

ab initio potential	masses	^{7}LiH	^{6}LiH	^{7}LiD	^{6}LiD
		RMS (cm^{-1})			
BO	nuclear	6.26	6.95	2.80	2.76
BO+DBOC	nuclear	2.24	2.66	1.29	1.19
BO+DBOC+β(R)	nuclear	1.79	2.14	1.18	1.15
BO+DBOC	atomic	0.91	1.22	1.01	1.07



Rotational spectra

Deviation of the calculated and empirical ro-vibrational constant as a function of vibrational quantum number[a)]



For 546 transitions (v=0-6, J=1-30): RMS (obs-cal) = 0.1041 cm^{-1}

a) $E(v,J) = E_v + B_v J(J+1) - D_v(J(J+1))^2 + H_v(J(J+1))^3 + L_v(J(J+1))^4 + \ldots$

Summary of the method used

The final spectrum includes:

- Born-Oppenheimer surface obtained at the MR-CISD+Q_P/6Z-56 level (BO)
- Diagonal Born-Oppenheimer Correction obtained at the MR-CISD/pw-CVTZ level (DBOC)
- relativistic correction obtained at the MVD level using icMRCISD/8-3-1 CAS/pw-CV5Z wave function (Rel)
- β function obtained at MR-CISD/pw-CVTZ level (Beta)

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